

21-4-60

German/Translation

Federal Republic of Germany
German Patent Office

Preliminary Published Application 2 035 730

International classification: C 08 g, 22/00

File number: P 20 35 730.6

Date of application: 18 July 1970

Date of publication: 27 January 1972

Applicant: Farbenfabriken Bayer AG, Leverkusen

Inventors:

Dr. Harro Witt, Dr. Gerhard Troemel and Gerhard Berndt

Title:

**PROCESS FOR PRODUCTION OF AQUEOUS SUSPENSIONS OR PASTES OF
FIBERLIKE CROSSLINKED PARTICLES AND THEIR USE**

Description

Great efforts have been made to produce replacement materials for textiles or leather from suspensions for synthetic materials on papermaking machines. It is known that synthetic staple fibers can be fabricated on papermaking machines. The resultant structures may be strengthened with resinous binders or by melting (cf. British patent 622 145 and US patent 2 721 139). These products have a paperlike character which makes them useless as substitutes for leather. Suspensions have also become known which can be fabricated on papermaking machines into flat structures or fabrics with the desired textile-like properties (DAS 1 282 436 and German OS 1 469 120). These suspensions are produced by a costly process in which organic synthetic polymers are exposed to high shearing forces in a suspending liquid.

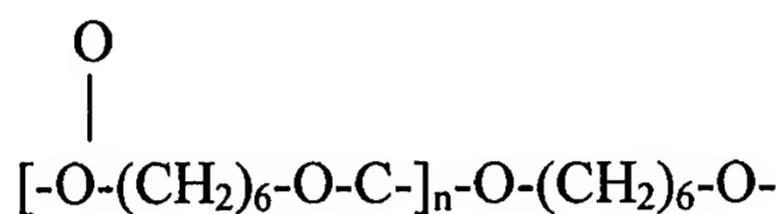
On the other hand a very simple process has become known for the production of aqueous sedimenting dispersions of polyaddition products. The latter consists in mixing polyurethanes and/or polyureas which contain ionic groups and free NCO groups with water in the presence of polyamines with more than two primary and/or secondary amino groups (German Patent 1 282 962). One obtains self-crosslinked particles of spherical to oblong shape. Dispersions with predominantly spherical particles are useless for fabrication on papermaking machines.

Flat structures produced by other fabrication techniques (e.g. by painting or pouring onto substrates) also have especially good properties if the shape of the particle deviates from spherical as much as possible. Another condition for good usage properties of flat structures, especially in the textile sector, is that the foils or coatings do not harden in the course of time. Thus dispersions could be produced with oblong particles and microporous foils from them whose initially very good properties vanished in the course of a few weeks as a result of hardening. Such dispersions are accessible, e.g. from ionic NCO prepolymers based on ethylene glycol-adipic acid polyesters.

As has now been surprisingly found it is possible to arrive at suspensions or pastes of markedly fibrous particles if prepolymers displaying both ionic groups and also free NCO groups, based on hexanediole-1,6-polycarbonates are brought to reaction with aqueous solutions of polyamines displaying at least three primary and/or secondary amino groups. The suspensions or pastes obtainable in this way permit the production of flat structures which display no hardening tendency although hexanediole-1,6-polycarbonates display a stronger crystallization tendency and a higher melting range than, for example, ethyleneglycol-adipic acid polyester. Another advantage of

the suspensions or pastes accessible in this way is the fact that they are exceptionally well suited for the production of flat structures, especially on papermaking machines.

The subject of the present invention is therefore a process for the production of aqueous suspensions or pastes of fibrous self-crosslinked particles by reaction both of polyurethane or polyurethane-polyurea prepolymers displaying both ionic groups and also free NCO groups with an aqueous solution of a polyamine displaying at least three primary and/or secondary amino groups, characterized by the fact that as prepolymers displaying both ionic groups and also free NCO groups those are used which consist to 60-90 wt.% of hexanediol-1,6-polycarbonate units of the general formula



where n is a whole number from 5 to 20.

The subject of the invention is also the suspensions or pastes which can be obtained by this process.

The subject of the invention is also the use of these suspensions or pastes for the production of flat structures, especially on the papermaking machine.

In an advisable variant of the process according to the invention one first produces an adduct from

- a) higher-molecular dihydroxy compounds containing hexanediol-1,6-carbonate groupings,
- b) compounds which contain besides at least one NCO group or at least one hydrogen atom reactive to isocyanates also at least one salt like group or group capable of salt formation,
- c) possibly other compounds with at least two hydrogen atoms capable of reacting with isocyanates, and

d) polyisocyanates in excess relative to the sum of all compounds reactive to isocyanates.

The term "higher molecular dihydroxy compounds containing hexanediol-1,6-carbonate groupings" here refers to preferably linear polycarbonates with molecular weight from 800 to 4000 which are accessible, for example, by reacting diphenyl carbonate with hexanediol-1,6 and possibly other low-molecular-weight dihydroxy compounds. The diol mixture used to build up the mixed polycarbonates should consist to at least 80 wt.% of hexanediol-1,6. The other diols represented to up to 20 wt.% may be, for example: pentanediol-1,5, octanediol-1,8, dodecanediol-1,12, methyl and dimethylpentanediol-1,5, methyl, dimethyl and trimethyl hexanediol-1,6, 1,6-hexanediol-mono and -bis-2-hydroxide ethyl ether, 1,6-hexanediol-mono or -bis-5-hydroxide caproic acid ester, adipic acid-bis-6-hydroxyhexyl ester, diethyleneglycol, tri- and tetramethylene glycol, oligomeric polyether of 1,2-propanediol with molecular weights up 700, 1,4-bis-hydroxymethyl-cyclohexane and hydroquinone-bis-2 hydroxyethyl ether.

The higher-molecular dihydroxy compounds displaying hexanediol-1,6-carbonate groupings are jointly used in the construction of the adducts in quantities such that the weight portion of these groupings in the prepolymer displaying ionic groups and NCO groups amounts to 60-90%.

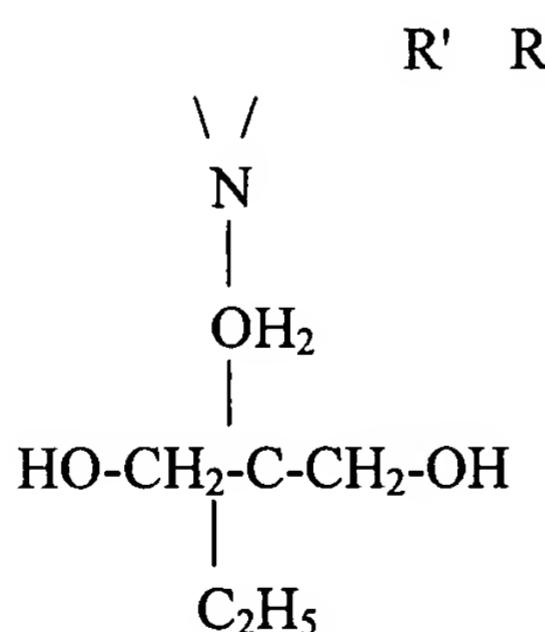
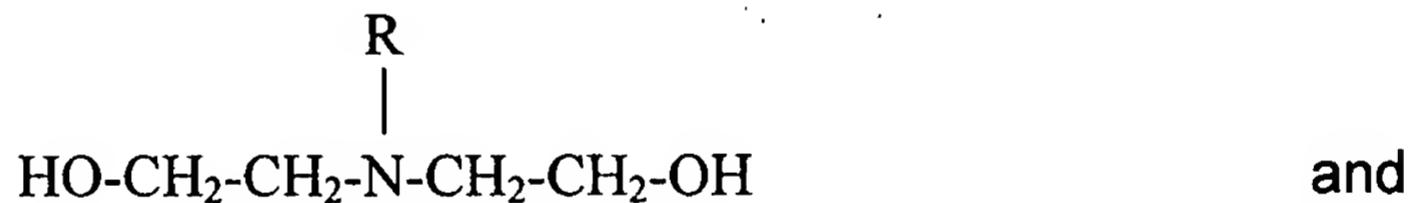
Preferably pure hexanediol-1,6-polycarbonates with molecular weights from 1000 to 2500 are used. In this case the content of hexanediol-1,6-polycarbonate groupings in the ionic NCO prepolymer is preferably 75-87 wt.%.

The components listed under b) through d) have already been described in German patent 1 282 962.

As compounds which besides at least one NCO group or at least one hydrogen atom reactive with respect to isocyanates also contain at least one saltlike group or group capable of salt formation for production of the adduct one preferably uses compounds which contain two groups reacting with isocyanates and one saltlike group or group capable of salt formation. The saltlike group may be of anionic or cationic nature. As an example of anionic lengtheners one can name compounds which besides two primary and/or secondary amino groups and/or two hydroxy groups also contain a sulfonate group or a carboxylate group. The compounds displaying saltlike groups or groups capable of salt formation are used jointly in such quantities that the adducts display a content of 0.01-1.5 wt.% of cationic or anionic groups.

Cationic lengtheners are preferably used which contain, besides two hydroxy groups, one tertiary amino group which may be transformed by alkylation into the corresponding ammonium salt. As representative of the large group of these compounds one can list two

aminodiols:



where R, R' and R" denote alkyl radicals with 1-4 C atoms.

However, one can also build up nonionic NCO-group-containing prepolymers first, therefore products which are constructed only from the components a, d and

possibly ? and subsequently ionically modify the formed prepolymer, e.g., by addition of carboxylic acid anhydrides, saltones, lactones, sulfur trioxide, sulfuric acid, amino epoxides, amino aziridines, bisulfite and similar compounds which are capable of reacting with one of the reactive groups present in the prepolymer, e.g., in the NCO group, the urethane or urea group, the aromatic nucleus of the diisocyanates, the olefinic double bond (e.g., by joint use of maleic acid anhydride, butenediol). The only essential feature for the process according to the invention is that the prepolymer contains cationic or anionic groups. Of what nature these groups are and how they are introduced plays no significant part.

As possibly jointly used compounds with at least two hydrogen atoms reactive to isocyanates all chain lengthening agents customarily used in polyurethane chemistry come into consideration. In particular here one can name the diols such as have already been named above as the initial components for the production of polycarbonates. Besides this one may use ethylene glycol, propylene glycol-1,2 and 1,3 and butanediol-1,2, -1,3, and 1,4. In addition in small quantities polyhydroxy compounds with more than two hydroxy groups may be added such as glycerin or trimethylol propane. Amino alcohols or diamines such as ethanolamine, ethylenediamine, propylenediamine-1,3 etc may also be used during the synthesis of the prepolymers used in the process according to the invention as chain lengtheners.

As polyisocyanates preferably one will use diisocyanates. Because of their better light stability aliphatic diisocyanates are preferred such as, for example, tetramethylene diisocyanate, hexamethylene diisocyanate, octamethylene diisocyanate, xylylene diisocyanates, 2,2,4- and/or 2,4,4-trimethylhexamethylene diisocyanate, 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate etc. The preferred diisocyanate

is hexamethylene diisocyanate. However, the usual aromatic isocyanates such as toluene diisocyanates, diphenylmethane diisocyanates, possibly in combination with conventional light stabilizers may also be used.

The ionic NCO prepolymer is produced by conventional methods: components a) through c) may be reacted simultaneously or successively with a polyisocyanate in the melt or in a solvent. The solvent should be inert with respect to isocyanates but may contain up to 2 wt.% water. The solvent should preferably be miscible with water and have a boiling point below 100°C at standard pressure.

In a preferred variant in the process according to the invention prepolymers displaying ionic groups and NCO groups are used for whose synthesis the excess of diisocyanate and the quantity of chain lengthening agent displaying two hydroxy groups and a tertiary amino group are selected such that the adduct has a content of free NCO groups of 1-4 wt.% and after the alkylation is completed a content of 0.02-0.2 wt.% of quaternary ammonium nitrogen.

The ionic NCO prepolymer is dissolved before dispersing preferably in a concentration of 30-60 wt.% in acetone. Such solutions at 50°C have viscosities of about 30-300 cP, preferably solutions of 50-200 cP are prepared.

These ionic NCO prepolymer solutions in acetone are mixed with aqueous solutions of polyamines with more than two primary and/or secondary amino groups. Following this the acetone is distilled off and one obtains the aqueous, sedimenting, redispersible suspensions. Polyamines with aliphatic amino groups, especially diethylene triamines, tetraethylene tetramine, tetraethylene pentamine and/or pentaethylene hexamine are preferred.

The mixing can be performed by adding the aqueous solution while stirring to the acetone or the acetone solution to the aqueous solution. This mixing is preferably conducted continuously by metering the two solutions into a mixing vessel by pumping.

The mixing vessel in the simplest case is provided with an agitator and an overflow through which the aqueous-acetone dispersion flows into a distillation apparatus. The dispersing temperature is between 20 and 60°C, preferably between 35 and 55°C. The weight quantity of water required for dispersing in which the polyamine is dissolved is 0.8-3 times, preferably 1-2 times the weight of the ionic NCO prepolymer. The ratio of amino groups to free NCO groups is between 0.2 and 1.5, in the case of continuous dispersing at 35-55°C preferably near the equivalent point.

The resulting aqueous, sedimenting, redispersible suspensions, consist of particles with a pronounced fiberlike structure crosslinked in themselves. The particle shape can be varied more or less selectively by the chemical structure of the polyadduct, by the dispersing temperature, the nature and the intensity of the intermixing and especially by the quantity of acetone and water.

Surprisingly with consideration of the process according to the state of the art, no higher shearing forces are necessary for the dispersing; normal low speed agitators are fully sufficient. Even when stirred by hand with a glass rod in the laboratory test the desired fibrous suspensions are obtained.

In this way fibrous particles can be obtained whose longitudinal dimension is more than 100 times as great as their cross diameter, e.g., 5 µ thick and more than 500 µ long. Such extremely fibrous particles cannot be used for all application purposes. Thus they are easily fabricated on papermaking machines but are difficult to blade. For bladable pastes particles of about 5-10 µ cross diameter and 15-150 µ length are better

suited. But even these suspensions can be fabricated very well on papermaking machines. The above noted dimensions naturally represent only approximate average values.

The suspensions accessible by the process according to the invention have a number of interesting fields of application. Of particular interest is the production of microporous coatings or foils. For this field of application the content of finely divided material whose particle shape approaches spherical should be as small as possible. The content of a suspension consisting of particles of less than 10 µm length or a ratio of length to cross diameter of less than 2 should if possible not exceed 20 wt.% of the solids.

Depending on the mode of fabrication the suspensions are applied in different dilutions. For poring or blading on substrates if necessary after the addition of various accessories, suspensions of 10-60% solid are used, in the blading process preferably a solid with a solids content of 30-50 wt.% are used. For fabrication on papermaking machines the solid concentration is less than 10%, preferably below 5%. Pouring or blading is performed by conventional methods. Layers can be applied to water-impermeable or water absorptive substrates and the latter after solidification be removed as self supporting textile structures. Microporous foils produced in this way can be glued, for example, on textiles, nonwovens or split leather. On the other hand these materials, however, can also be coated directly with the suspensions. In both cases it is often advantageous to add conventional thickeners to the suspension, especially in order to assure good spreadability.

On the other hand, flat structures can be deposited on screens from dilute, aqueous suspensions. For example, the Rapid-Köthen sheet former or papermaking

machines are suitable for this. The property pattern of the flat structures can be varied by additions of synthetic stable fibers and/or cellulose. In this case other additives such as wetting agents or dispersions of polymers, polycondensates or polyadducts, especially polyurethanes may also be used. The dispersions are coagulated on the screen in the suspension before deposition. The flat structures can be solidified independently of the method of their production in various ways. Usually they are already self-supporting after drying at room temperature. The mechanical scores can be improved by a temperature or pressure treatment. This improvement is usually at the expense of water vapor permeability. A sintering process is preferably achieved by a temperature pulse -- e.g. three minutes at 180°C (cf. French patent 1 576 476). The pressure treatment can be performed if necessary on warm calendars, in which case the foil can be simultaneously embossed.

Brushable and bladable pastes are especially important, which are produced from the initially present sedimenting redispersible suspensions by decanting, addition of thickeners such as alginates, soluble cellulose derivatives or hydrophilic oligo- or polyurethane colloids. After prolonged storage no sedimentation takes place any longer in these pastes.

To produce coatings of low water vapor permeability but of outstanding mechanical properties, e.g., abrasion and crease resistance and hydrolysis stability, these pastes may contain 5-70%, preferably 5-40% of stable polyurethane dispersions, preferably polyurethane ionomer dispersions with particle sizes between 0.2 and 2 µm. The combinability of cationic fiber suspensions with anionic stable dispersions and vice versa is especially advantageous.

The suspensions (pulps) produced for fabrication on the papermaking machine are also added for modification and improvement of the initial strength of the wet state, preferably stable polyurethane dispersions. In this case cationic dispersions are deposited preferably on staple fibers, anionic dispersions, preferably on cationic polyurethane ionomer fibers.

By variation of temperature, pressure and duration of the sintering process practically any desired degree of water vapor permeability can be selectively adjusted. In the case of low water vapor permeability extremely high tensile and abrasion resistances are achieved. In particular on an initially isotropic material zones of different water vapor permeability and strength can be created so that the material can be optimally adjusted to its later application purpose.

Especially advantageous in the case of microporous coatings with the dispersions according to the invention compared to coatings according to the state of the art is the combination of the following properties:

- High strength
- Low abrasion
- No yellowing
- High hydrolysis resistance
- High water vapor permeability can be reduced by secondary treatment optionally with an increase in strength
- Solvent resistance
- Total absence of organic solvents during coating process

As additives for fabrication on papermaking machines in particular staple fibers of polyamide, polyester, polyacrylonitrile, polyurethane elastomers etc. come into consideration.

Before they are fabricated into flat structures the suspensions can also be provided with crosslinking agents (cf. French patent 1 584 515). For example, capped

isocyanates, formaldehyde or formaldehyde derivatives come into consideration. With such crosslinking agents the suspension particles can be crosslinked with each other in the foil. The flat structures can be dyed or pigmented and be provided with a finish according to known methods.

The flat structures according to the invention represent extremely valuable synthetic materials with a leatherlike or textile-like character. They are used, for example, as respiration-active clothing, e.g., for foul weather clothing and rain clothing, for the production of shoes, especially as shoe top leather and as sole material, for the production of upholstery/seat cover materials, e.g. for car seats and couches, for the production of belts and watch bands, solvent-resistant filter cloths. For these application fields both flat structures produced only from the dispersion provided with additives according to the invention, e.g., on the papermaking machine are suitable as well as those which were obtained by conventional process techniques such as gluing, flame lamination or coating of water vapor-permeable substrates such as bound fiber nonwovens, textiles, split leather with the dispersions according to the invention.

A: Examples of the production of suspensions

Example 1

1000 g of a hexanediol-1,6-polycarbonate with the OH number of 60.8 are stirred at 120°C for 1 h with 159 g of hexamethylene-1,6-diisocyanate. The melt is allowed to cool to 60°C and a solution of 8 g of N-methyldiethanolamine in 236 g of acetone is added. One stirs for an additional two hours at 60°C and allows to stand over night. One dilutes with simultaneous quaternization with 8.3 g of dimethyl sulfate at 50°C with acetone to a prepolymer content of 41 wt.%. This solution has an NCO content of 0.89% and a viscosity of ca. 100 cP at 50°C.

A metering pump conveys simultaneously per minute 70 g of the ionic prepolymer solution of 50°C and 54 g of a 60°C warm aqueous solution of 0.532 g of diethylene triamine in a vessel provided with an overflow in which a propeller agitator is running at 300-400 revolutions per minute. The volume up to the overflow amounts to ca. 400 ml. The temperature in the dispersing vessel is between 40 and 45°C. The aqueous-acetone dispersion flows through the overflow into a distillation apparatus in which the acetone is driven off at a bath temperature of 90°C with stirring. The result is an aqueous sedimenting dispersible suspension of fibrous particles with transverse diameters of about 5 μ and longitudinal diameters of 20-120 μ , in isolated cases up to 500 μ . The suspension is insoluble in hot dimethylformamide.

Example 2

The 41% prepolymer solution and the type of dispersing are the same as in example 1. Each minute again 70 g of prepolymer solution, but now 71.7 g of aqueous solution of 0.532 g of diethylene triamine are conveyed. The particles of the suspension display an extremely pronounced fibrous character with cross diameters of less than 5 μ and lengths of a few 100 μ .

Example 3

1000 g of the above used hexanediol-1,6-polycarbonate are reacted as in example 1 with 173 g of hexamethylene-1,6-diisocyanate and 8 g of N-methyldiethanolamine, quaternated with 8.3 g of dimethyl sulfate and diluted with acetone to a prepolymer content of 48.4%. This solution has a NCO value of 1.34% and at 50°C a viscosity of ca. 110 cP. As in example 1 per minute 69.1 g of prepolymer solution are mixed with 56 g of an aqueous solution of 0.775 g diethylene triamine. After the acetone is distilled off one obtains a suspension of particles insoluble in

dimethylchloramide of about 5 μ thickness and 10-100 μ length, in individual cases up to 400 μ length. The suspension contains less than 5 wt.%, relative to the solid, of smaller spherical particles of 5-10 μ diameter which can be removed by sedimentation or screening.

Example 4

As in example 1, 1000 g of hexanediol-1,6-polycarbonate (OH number 60.8) are reacted with 153 g of hexamethylene-1,6-diisocyanate and 8 g of N-methyldiethanolamine and with quaternation with 8.3 g of dimethyl sulfate diluted to a prepolymer content of 45% with acetone. This solution has an NCO content of 0.87% and a viscosity at 50°C of ca. 120 cP.

Per minute as in example 1 63.5 g of prepolymer solution are mixed with 33.2 g of an aqueous solution of 0.453 g of diethylene triamine. The result is an aqueous suspension of particles insoluble in dimethylformamide of ca. 5 μ m cross diameter and 10-300 μ m longitudinal diameter.

Example 5

1000 g of a hexanediol-1,6-polycarbonate of OH number 37 are reacted as in example 1 with 121 g of hexamethylene-1,6-diisocyanate and 7.7 g of N-methyldiethanolamine, quaternated with 8 g of dimethyl sulfate and diluted with acetone to a prepolymer content of 45%.

72 g of this solution are mixed per minute with 45.3 g of an aqueous solution of 0.587 g of diethylene triamine. The resulting aqueous suspension resembles that produced in example 3.

Example 6

1000 g of a hexanediol-1,6-polycarbonate of OH number 52.8 are reacted as in example 1 with 180 g of hexamethylene-1,6-diisocyanate and 16 g of methyldiethanolamine and quaternated with 16.6 g of dimethyl sulfate. The 40% solution of this polymer in acetone has an NCO content of 1.16% and a viscosity of ca. 40 cP at 50°C.

The dispersing is performed as in example 1 by mixing per minute 74.0 g of the prepolymer solution and 41.4 g of an aqueous solution of 0.7 g of diethylene triamine. The suspension corresponds approximately to that of example 3, but the particles are somewhat smaller.

Example 7

29380 g of hexanediol-1,6-polycarbonate (OH number 52.8) to which 29.4 g of 1,1,1-tris-[hydroxymethyl]-propane are added are stirred for 1 h with 3901 g of hexamethylene diisocyanate at 120°C. At 60°C the solution of 231 g of N-methyldiethanolamine in 6800 g of acetone is added and the stirring continued for another 5 hours at 60°C. After diluting with acetone to a prepolymer content of 39% it is quaternated with 240 g of dimethyl sulfate. This solution has an NCO value of 0.58%, a viscosity of ca. 120 cP at 50°C. As in example 1 per minute 70.5 g of prepolymer solution are mixed with 38.5 g of an aqueous solution of 0.336 g of diethylene triamine. The suspension which is insoluble in hot dimethylformamide displays a relatively nonuniform particle pattern: besides very few (less than 3%) spherical particles there is a small portion (less than 20%) in the form of rods of ca. 5 µm diameter and 10-30 µm length. The greater part consists of small fibers with lengths up to 150 µ, in solitary cases up to 500 µ.

Examples 8-13

1000 g each of hexanediol-1,6-polycarbonate are mixed with hexamethylene-1,6-diisocyanate (HDI) for 30 min at 100°C and stirred. Then various quantities of different low-molecular diols are stirred in and held for another 30 min at 100°C. The batch is allowed to cool to 60°C, a solution of N-methyldiethanolamine (MDA) in 275 g of acetone is added in drops and allowed to stand over night. Table 1 reports the quantities of the components and the OH number of the polycarbonate.

Table 1

| No. | OH number | HDI [g] | Diol | g | MDA [g] |
|-----|-----------|---------|------------------------------------|-------|---------|
| 8 | 57.8 | 175 | Butandiol-1,4 | 10.2 | 8.2 |
| 9 | 57.8 | 186.5 | Hexanediol-1,6 | 20.8 | 8.33 |
| 10 | 57.8 | 172 | Neopentylglycol | 10.2 | 8.16 |
| 11 | 57.8 | 212 | Neopentylglycol | 32.2 | 8.6 |
| 12 | 57.8 | 164 | 1,4-bis-(β-hydroxy-ethoxy)-benzene | 10.1 | 8.1 |
| 13 | 52.8 | 198 | Octaethylene glycol | 100.0 | 8.0 |

From Table 2 one sees the prepolymer content to which one dilutes with acetone (% prep.), with how much dimethyl sulfate the quaternation is then performed (DMS) and what NCO values (% NCO) and viscosities (at 50°C) these solutions have. The solutions are mixed as in example 1 with aqueous diethylene triamine solutions at 40-45°C. In the last three columns the quantities of prepolymer solution (prep), aqueous amine solution (W) and a diethylene triamine (DAET) are given which are conveyed per minute.

Tabl 2

| No. | DMS g | % Prep | % NCO | Vis. cP | Prep g | W g | DAT g |
|-----|-------|--------|-------|---------|--------|------|-------|
| 8 | 8.5 | 46.5 | 0.94 | 150 | 72.2 | 40.8 | 0.566 |
| 9 | 8.65 | 45.0 | 0.865 | 130 | 72.4 | 39.1 | 0.512 |
| 10 | 8.46 | 46.0 | 0.905 | 130 | 72.5 | 46.7 | 0.535 |
| 11 | 8.9 | 50.0 | 1.00 | 190 | 73.6 | 51.5 | 0.600 |
| 12 | 8.4 | 47.0 | 0.955 | 145 | 73.5 | 48.4 | 0.573 |
| 13 | 8.3 | 50.0 | 1.33 | 80 | 74.9 | 59.9 | 0.815 |

The resulting suspensions correspond approximately to those in example 7.

Example 14

1000 g of a polycarbonate of OH number 59.5 produced by reaction of the reaction product of hexanediole-1,6 with adipic acid (molar ratio 5:1) with diphenylcarbonate are reacted as in example 1 with 160 g of hexamethylene-1,6-diisocyanate and 8 g of N-methyldiethanolamine and quaternated with 8.3 g of dimethyl sulfate. The 48% acetone prepolymer solution has an NCO value of 1.12 and a viscosity of 200 cP at 50°C. Per minute as in example 1 73.5 g of prepolymer solution are mixed [with] 0.69 g of diethylene triamine. A suspension of fiber like particles is formed which are insoluble in dimethylformamide.

Example 15

A modified hexanediol-1,6-polycarbonate is synthesized by known methods as described in Belgium patent 731 926 as follows:

Hexanediole-1,6 is reacted with caprolactone in a molar ratio of 5:1 and then esterified with diphenyl carbonate while distilling off phenol until an OH number of 112 is reached. 1000 g of this polycarbonate are reacted as in example 8-13 with 300 g of hexamethylene-1,6-diisocyanate, 34.6 g of neopentylglycol and 9.2 g of N-

methyldiethanolamine. The prepolymer is quaternated with 9.5 g of dimethyl sulfate and diluted with acetone to 45%. As in example 1 per minute 73.0 g of this prepolymer solution are mixed with 45.9 g of an aqueous solution of 0.477 g of diethylenetriamine. The suspension corresponds approximately to that of the example 7.

Examples of application of the suspensions

Example 16

100 g of a 35% suspension as per example 4 are mixed with 4 g of a thickener composed of 2 g of water, 1 g of a polyurethane adduct from 2 moles of polyethylene glycol ether of molecular weight 6000, 1 mole of 2,4-toluene diisocyanate and two moles of stearyl isocyanate as well as one g of a condensation product from benzyl chloride and oxydiphenyl with 12 moles of ethylene oxide (benzyl-p-oxydiphenyl polyglycol ether). By stirring a highly viscous paintable paste is obtained which is applied by a suitable blading device with a film thickness of 0.8 mm to a highly lustrous chrome-plated metal sheet. By drying this layer for 30 min in a drying cabinet (type Heraeus LKTFU) using convection at 80°C a 0.35 mm thick porous foil is obtained which, after cooling to room temperature (25°C), can be removed from the metal plate without cracking. The measurement of tensile strength and tearing elongation per DIN 53504 when measured on standard rods with a cross bar width of 5.1 mm gave the values listed under 80°C. By a secondary heat treatment for 5 min at 180°C the values listed under the column head 180°C were obtained.

| | 80°C | 180°C |
|---------------------|-----------------------|------------------------|
| Tensile strength | 80 kp/cm ² | 114 kp/cm ² |
| Elongation at break | 300% | 380% |

These values did not change after aging for six days at 95% relative humidity and temperatures of $70\pm2^\circ\text{C}$. The water vapor permeability of the foil dried at 80°C was $500 \text{ g/m}^2\cdot\text{day}$, after heat treatment at 180°C , $350 \text{ g/m}^2\cdot\text{day}$. The water vapor permeability was determined according to DIN 53122 at a humidity difference of 85% relative humidity and 20°C test temperature.

Example 17

A paste produced according to example 16 from a suspension from example 3 and thickener is applied to a bleached cotton-nettle fabric of 80 g per square meter with a suitable device consisting of a tentor frame and a blading device with a uniform film thickness of 0.3 mm and dried in the convection dryer at 80°C for 8 min. The coating obtained is porous and can be bent sharply without breaking. The total weight is 180 g/m^2 . The porous film has an adhesive strength 1 kp/cm in the peeling test at a separation rate of 10 cm/min. In the tearing test according to example 16 for the foil separated from the textile a tensile strength of 40 kp/cm^2 was obtained. By secondary treatment for three min at 180°C the tensile strength was increased to 80 kp/cm^2 . In the case of a coating sample also heated for three min at 180°C the porous film could no longer be separated flawlessly since the strength of the adhesion to the textile was too great.

The coated fabric allows the passage of $620 \text{ g/m}^2\cdot\text{day}$ of water vapor at 80% relative humidity difference and 25°C according to DIN 53379.

The coating is resistant to 100000 folds without cracking when tested per DIN 53359. After storage for 4 weeks at room temperature no increase in hardness or of the coating is observed. The coating is suitable for the production of a leather substitute that is permeable to air and water.

Example 18

1000 g of a suspension according to example 3 are mixed with a mixture of 50 g of the thickener mentioned in example 16 of polyurethane and ethoxylated condensation product as well as 5 g of iron oxide brown colored pigment. The paste obtained has a viscosity of about 100 poise/25°C and is applied to a chromed metal sheet in a film thickness of about 0.8 mm. A cotton round loom knit product with a qm weight of 120 is placed on the still moist film and the composite substance is dried for 10 minute at 100°C. After drying it is heated secondarily to 170°C for 5 min and the composite material cooled with the sheet to room temperature and detached from the sheet. A porous composite material is obtained weighing 480 g/m² which is highly flexible and resistant to bending. The uniformly colored material does not change its flexibility after 4 weeks of storage. The water vapor permeability per DIN 53122 is 500 g/m²·day at a moisture difference of 80% relative humidity and 25°C test temperature.

Example 19

A brushing paste is prepared from a suspension according to example 7 in the same manner as described in example 18 and coated in a coating machine using a rubber cloth blading device onto a so called release paper. For this a paper coated with polyethylene was used such as is used for the production of milk cartons. The film is dried for 5 min at 100°C and wound up. This film is glued in a second operating step with a commercial solvent adhesive based on polyurethane to a textile. For this purpose a roller applicator mill was used and the adhesive was applied with a quantity corresponding to 20 g/m² of solids to the porous foil to be glued and joined to a cotton knit product under light rolling pressure of 10 kp/m linear and dried. The composite

material after the hardening of the glue is pulled off the release paper and secondarily treated for 5 minutes at 170°C.

Part of the sample acquires a suitable finish with a dyed leather finishing agent, achieving a leatherlike surface character with simultaneous coloring. Stronger influencing of the air and water vapor permeability of the porous film is avoided by applying the finishing coating by spraying at a rate of less than 10 g/m².

The coatings have the following properties in the tests customarily performed in the leather industry.

| | Damage with finish | Damage without finish |
|--|--------------------|---|
| Rubbing fastness hot per SATRA | none | traces |
| Hot iron resistance at 150°C | traces | distinct |
| Bending resistance (dry) 2000 bends | traces | traces |
| Water vapor permeability (per IUP) (per DIN 53122) | 3.7 590 | 8.5 mg/h·cm ² 660 g/m ² ·day |

The rubbing fastness hot was determined with a dry felt with 300 revolutions at 2.5 kg load without cooling of the test body. In the hot iron resistance test the body was loaded at 150°C over a rectangular edge with a pressure of ca. 0.75 kp. The bending crease resistance was tested in the Bally flexometer apparatus.

Both coatings were subjected to a technical chemical cleaning five times. Appearance and porosity measured by the water vapor permeability were unchanged after this.

Example 20

1000 g of a 40% suspension per example 9 were stirred into a paintable paste with 30 g of the thickener listed in example 1 of polyurethane adduct and ethoxilated condensation product diluted with 30 g of water and painted onto a metal plate according to example 16. The adjustment of the gap was 1.4 mm. After drying at 80°C and secondary heating to 160°C for 5 minutes a crack-free 0.6 mm thick foil resulted. A water vapor permeability of 650 g/m²·day was determined per DIN 53122 at a moisture difference of 85% relative air humidity at 25°C.

Example 21

In the same manner as described in example 20 a 40% suspension per example 12 was made into a porous film and secondarily heated at 160°C for 5 min. The tensile strength test showed 70 kp/cm² at 420% breaking elongation. The 0.6 mm thick foil under the conditions of example 20 had a water vapor permeability of 400 g/m²·day.

Example 22

50 g of the dispersion produced according to example 7 (40%) are formed into a sheet in the Rapid-Köthen sheet former after addition of 6 liters of water and dried for 5 minutes at 90°C under a pressure of 1 kg/cm². The elastic microporous foil has a tensile strength (DIN 53504) of 36 kp/cm² at a breaking elongation of 470% and a water vapor permeability of 675 g/m²·day (DIN 53122) at a thickness of 0.7 mm. After six days of aging at 70°C and 95% relative humidity the tensile strength increased to 83 kp/cm² at 520% breaking elongation. By additional heat treatment for three min at 170°C the following values were obtained

| | |
|--|---------------------------|
| Tensile strength | 47 kp/cm ² |
| Elongation at break | 490% |
| Water vapor permeability | 600 g/m ² ·day |
| After 6 days at 70°C and 95% relative humidity | |
| Tensile strength | 75 kp/cm ² |
| Elongation at break | 540% |

The foils withstand 100000 bends (Bally flexometer) without damage.

Example 23

Using the sedimented dispersion (40%) produced in example 7 a nonwoven was prepared on a Fourdrinier long screen laboratory papermaking machine (Kämmerer type) which had a leatherlike character after leaving the papermaking machine. The following process was used:

2200 g of the above dispersion were provided with 4 l of water. To it while stirring slowly 20 cm³ of a 50% chlorobutadiene latex were added which subsequently was brought to coagulation with 50 cm³ of a 2% aqueous solution of a cationic polyamide-polyamine-epichlorhydrin product which usually serves for wet strength finishing of pulp papers. The suspension was then fed into 100 g of a polyester short cut fiber (6 mm 3.3 dtex) and thoroughly mixed. 195 l of water were added in a V2A steel mixing vat and the mixture was fabricated on the above noted machine by the method known from paper fabrication into a nonwoven. The first drying cylinder was held at 80°C. It resulted in a ca. 0.8 mm thick flat structure which after 3 minutes of tempering at 140°C had a water vapor permeability of 10.4 mg/h·cm² (IUP) and at 160°C of 6.6 mg/h·cm² (IUP).

Example 24

The procedure used in example 23 was followed, but instead of polyester short cut fibers 50 g of a polyamide short cut fiber (6 mm 2.7 dtex) were used. The flat structure resembled that of example 23.

Example 25

2200 g of the sedimenting dispersion prepared in example 7 (40%) are provided with 3.5 l water. To this dispersion then while stirring slowly 20 cm³ of a 45% anionic acrylic acid butyl ester latex are added which was coagulated out with 50 cm³ of a 1% aqueous solution of a cationic condensation product of formaldehyde and aliphatic aminocarboxylic acids. Following this 25 g of bleached spruce sulfite pulp and 500 cm³ of water was added to the suspension and thoroughly mixed. Before the mixture was fabricated into a nonwoven by known methods on the laboratory papermaking machine described in example 23, it was provided with 192 l of water in a V2A steel mixing vat. The resulting nonwoven after heat treatment for three min at 140°C and 160°C had a water vapor permeability of 3.6 mg/hcm² (IUP).

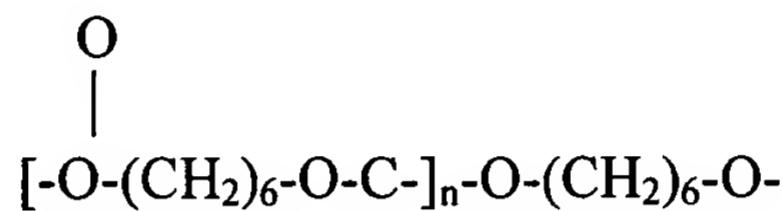
Example 26

The laboratory papermaking machine mentioned in example 23 was used in the following trial with a steep screen (20°C) and a secondary pulp spreader. While on the steep screen a (by known processes) nonwoven of polyester short cut fibers (15 mm, 3.3 dtex) was prepared, the secondary pulp charge was prepared with a suspension consisting of 2200 g of the dispersion (40%) prepared according to example 7, 20 cm³ of a 50% anionic butadiene-acrylonitrile latex which had been brought to coagulation with 50 cm³ of a 2% aqueous solution of a cationic polyamide-polyamine-epichlorhydren product.

The separately prepared nonwovens brought together on a Gautsch roll had an area structure consisting of a chemical fiber nonwoven as the support and a foil lying on it. The passage through the drying part of the laboratory papermaking machine was performed as stated in example 23.

Claims

1. Process for the production of aqueous suspensions or pastes of fiber-like self-crosslinked particles by reaction of polyurethane or polyurethane-polyurea prepolymers displaying both ionic groups and also free NCO groups with an aqueous solution of a polyamine displaying at least three primary and/or secondary amino groups, characterized by the fact that as prepolymers displaying both ionic groups and also free NCO groups those are used which consist to 60-90 wt.% of hexanediol-1,6-polycarbonate units of the general formula



where n is a whole number from 5 to 20.

2. Process as in Claim 1 characterized by the fact that the prepolymers displaying both ionic groups and free NCO groups are brought to reaction in the form of a 40-70% solution in acetone with the aqueous polyamine solution.
3. Process as in Claims 1 or 2 characterized by the fact that as the prepolymer displaying both ionic groups and free NCO groups one is used which displays 1-4 wt.% of free NCO groups.
4. Process as in Claims 1 - 3 characterized by the fact that as the prepolymer displaying both ionic groups and free NCO groups one is used which contains 0.02-0.2 wt.% of quaternary ammonium nitrogen.
5. Process as in Claims 2 - 4 characterized by the fact that the components are continually mixed at 20-60°C in order to cause reaction of the prepolymer dissolved in acetone with the polyamine dissolved in water.
6. Process as in Claims 1 - 5 characterized by the fact that the prepolymer is brought to reaction with the polyamine in an NH/NCO ratio of 0.2-1.5.

7. Process as in Claims 1 - 6, characterized by the fact that the weight ratio of the water used to dissolve the polyamine to the quantity of free polymer is 0.8-3.
8. Suspensions or pastes obtained according claims 1-7.
9. Application of the suspensions or pastes produced according to claims 1-7 for the production of flat structures.
10. Application as in Claim 9 characterized by the fact that the aqueous suspensions if necessary after addition of conventional thickeners and/or crosslinking agents are poured or bladed onto substrates and dried at temperature from room temperature up to 200°C.
11. Application as in Claim 9 characterized by the fact that porous structures are produced on the papermaking machine from the suspensions, if necessary after dilution with water.
12. Application as in Claim 11 characterized by the fact that suspensions are used which contain additives of synthetic staple fibers and/or cellulose.
13. Application as in Claim 11 characterized by the fact that the suspensions are used in a mixture with dispersions of polymers and/or polycondensates and/or polyadducts.
14. Application as in Claim 11 characterized by the fact that the aqueous suspensions or pastes contain 5-70% of stable polyurethane ionomer dispersions.